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Discussion Section:

Exam #2
Biophysical Chemistry
Chemistry 130A
Fall 1999

Show all your work

State your assumptions and check that they hold

Information Page

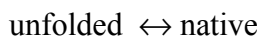
$$R = 8.3145 \text{ J/(K mol)} = 0.08206 \text{ L atm / (K mol)}$$

$$F = \text{Faraday's constant} = 9.6485 \times 10^4 \text{ C/mol}$$

Oxidant/Reductant	Electrode Reaction	Reduction Potentials	
		$\mathcal{E}^{\circ}(\text{V})$	$\mathcal{E}^{\circ'}(\text{V})$
NAD^+/NADH	$\text{NAD}^+ + \text{H}^+ + 2\text{e}^- \rightarrow \text{NADH}$	-0.105	-0.320
$\text{H}^+/\text{H}_2/\text{Pt}$	$2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{H}_2(\text{g})$	0.0	-0.421
Ag^+/Ag	$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}(\text{s})$	0.799	
Fe^{2+}/Fe	$\text{Fe}^{2+} + 2 \text{e}^- \rightarrow \text{Fe}(\text{s})$	-0.4402	

Reaction	ΔG° kJ/mol
D-Glucose -6-Phosphate \rightarrow D-Fructose-6-Phosphate	1.7
Pyruvate + NADH + $\text{H}^+ \rightarrow$ Lactate + NAD^+	-25.1
ATP + $\text{H}_2\text{O} \rightarrow$ ADP + Phosphate	-31.0
2-Phosphoenolpyruvate + ADP \rightarrow Pyruvate + ATP	-31.4

1. (20 pts) Consider a protein folding equilibrium,



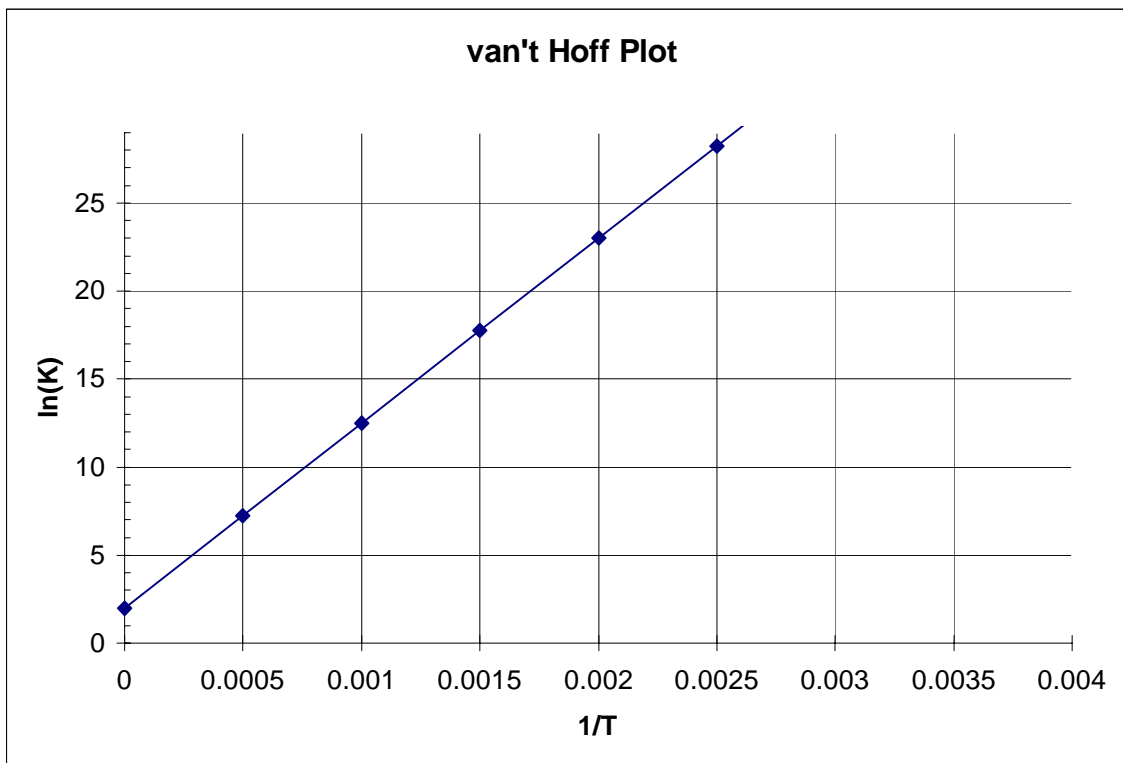
(a) (5 pts) Experimentally, we know that heating a protein denatures it, i.e. as the temperature increases, [unfolded] increases. Assuming ΔH° and ΔS° are independent of temperature over the range considered, what does this imply about the sign of ΔH° for the folding reaction?

There are a number of ways of answering this problem. The intuitive way is to invoke LeChâtelier's principle that implies that as you add heat to the native state it unfolds. So that the folding reaction must release heat, thus the reaction is exothermic and ΔH° must be negative. More formally we can use the temperature dependence of the equilibrium constant

$$\ln(K_2/K_1) = -(\Delta H^\circ/R)(1/T_2 - 1/T_1)$$

Since $(1/T_2 - 1/T_1) < 0$ and $K_2 < K_1$ so $\ln(K_2/K_1) < 0$, ΔH° must be less than zero to account for the signs.

Suppose that after we ran the temperature-dependence experiments, we found



(b) (10 pts) What are ΔH° and ΔS° for this equilibrium? (Again assume that they're constant over the temperature range considered.)

Here we can use the equation

$$\ln(K_2/K_1) = - (\Delta H^\circ/R)(1/T_2 - 1/T_1)$$

in combination with the definition of ΔG°

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$$

Reading off the graph we use:

$$1/T_1 = 0.0005$$

$$1/T_2 = 0.001 \quad (\text{Man, those are high temps!})$$

$$\ln(K_1) = 7$$

$$\ln(K_2) = 12.5$$

So by the first equation

$$12.5 - 7 = - (\Delta H^\circ/R)(0.001 - 0.0005)$$

$$5.5 = - (\Delta H^\circ/R)(0.0005)$$

Solving for ΔH° : $\Delta H^\circ = -91.5 \text{ kJ/mol}$

(c) (5 pts) What is the chemical potential at 37 °C for this system at equilibrium?

The first thing to do is note that the chemical potential, $\Delta\mu$, for this system is equivalent to ΔG since we quote everything in kJ/mol. ($\Delta\mu$ is the molar free energy) The second is to remember that at equilibrium, ΔG is zero. Now, ΔG° , is not zero, nor is $\Delta\mu^\circ$. But we didn't ask for that.

2. (10 pts) Consider the equilibrium in which a heme protein, P , binds a Fe^{+2} ion from solution:



(a) (5 pts) If we put 1 micromolar (ie 1.0×10^{-6} M) $P \bullet \text{Fe}^{+2}$ into water, what is $[P]$ at equilibrium, assuming an ideal solution?

Assuming an ideal solution, the equilibrium constant for the association reaction is:

$$K = [P \bullet \text{Fe}^{+2}] / [P][\text{Fe}^{+2}]$$

Setting the concentration of free protein at equilibrium equal to x , and using the total protein concentration, $P_0 = 1.0 \times 10^{-6}$ M we find that

$$K = P_0 - x / (x \cdot x)$$

(Remember that $[P] = [\text{Fe}^{+2}]$ since all the iron came from the salt.) At this point one can make the assumption that $x \ll P_0$ or solve the quadratic equation. The former way is a lot easier.

$$x \cdot x = P_0 / K = 1.0 \times 10^{-6} / 5.0 \times 10^{12} = 0.2 \times 10^{-18}$$

$$x = 4.47 \times 10^{-10} \text{ (Which is much smaller than micromolar)}$$

The quadratic equation gives the same answer.

(b) (5 pts) For the same solution as in part (a), suppose we find that, in the real solution, $[P] = 6.0 \times 10^{-10}$ M, and have measured that the activity coefficient of the protein doesn't change upon uptake of the Fe^{+2} ion. What is the activity coefficient for the Fe^{+2} ion?

The equilibrium constant for the non-ideal solution is:

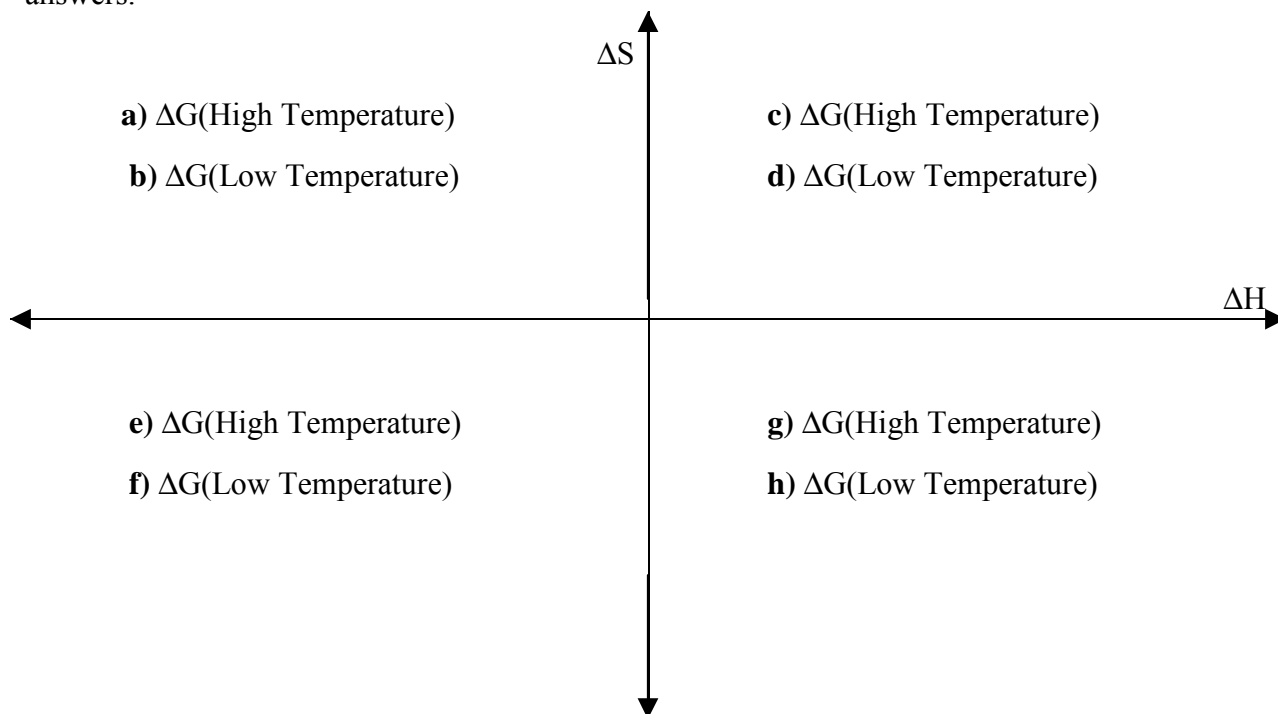
$$K = \gamma_{PFE} [P \bullet \text{Fe}^{+2}] / \gamma_P [P] \gamma_{FE} [\text{Fe}^{+2}]$$

We are given that $\gamma_{PFE} = \gamma_P$, and that $[P] = [\text{Fe}^{+2}]$ and that $[P] \ll P_0$, so

$$K = [P \bullet \text{Fe}^{+2}] / [P] \gamma_{FE} [\text{Fe}^{+2}] = P_0 / x \gamma_{FE} x = 5.0 \times 10^{12}$$

Solving for γ_{FE} with $P_0 = 1.0 \times 10^{-6}$ M and $x = 6.0 \times 10^{-10}$ M gives $\gamma_{FE} = 0.56$

3. (10 pts) Predict the sign of ΔG under the various conditions on the graph. Justify your answers.



For each of a-h and the origin ($\Delta H = \Delta S = 0$) indicate your choice of sign for ΔG and state why.

For this we use the equation $\Delta G = \Delta H - T\Delta S$

a) $\Delta G < 0$ ($\Delta H < 0$ & $T\Delta S$ positive)

b) $\Delta G < 0$ ($\Delta H < 0$ & $T\Delta S$ positive)

c) $\Delta G < 0$ ($\Delta H > 0$ but positive $T\Delta S$ dominates)

d) $\Delta G > 0$ ($\Delta H > 0$ dominates & $T\Delta S$ small)

e) $\Delta G > 0$ ($\Delta H < 0$ but negative $T\Delta S$ dominates)

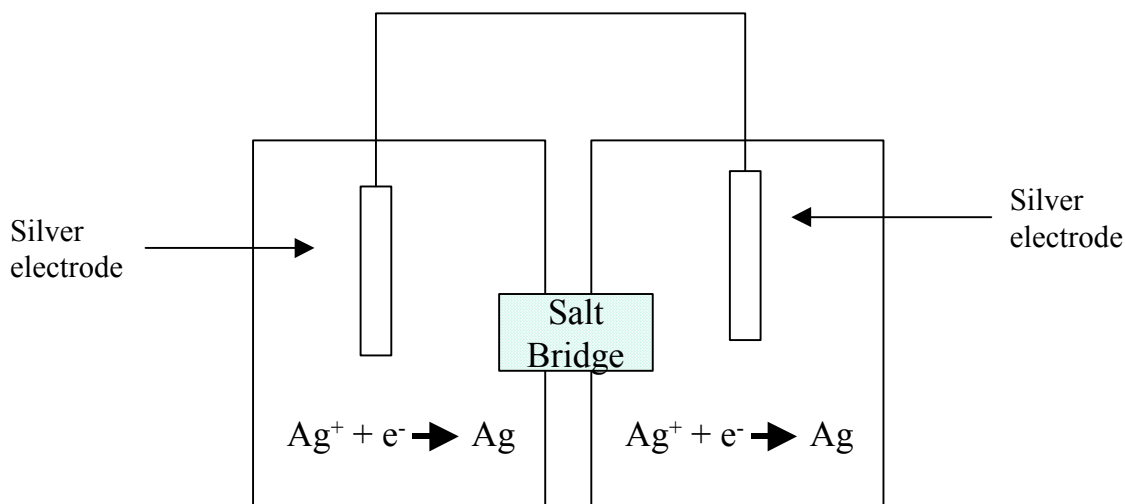
f) $\Delta G < 0$ ($\Delta H < 0$ & $T\Delta S$ small)

g) $\Delta G > 0$ ($\Delta H > 0$ & negative $T\Delta S$)

h) $\Delta G > 0$ ($\Delta H > 0$ & negative $T\Delta S$)

Origin: $\Delta G = 0$ since both ΔH and ΔS are zero.

4. (20 pts) Consider the following galvanic cell:



Answer the following questions using the data on the page of tables. Assume we are running the reaction at 25 °C.

(a) (5 pts) What is the equilibrium constant for the reduction of silver ion.

The equilibrium constant is found from the equation:

$$\mathcal{E}^{\circ} = (RT/nF)\ln(K)$$

From the table:

$$0.799\text{V} = (8.3145 \cdot 298 / 96485) \ln(K)$$

Solving for K gives

$$K = 3.26 \times 10^{13}$$

(b) (15 pts) If the concentration of silver ion in the left cell is 0.01M and the concentration of silver ion in the right cell is 0.1M, do electrons flow in this circuit? That is, is there a potential difference between the two half-cells? If so, what is it?

Here we right down the two half reactions and their Nernst equations.

$$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag(s)} \quad \mathcal{E} = 0.799\text{V} - (RT/F)\ln(X_{\text{Ag}}/[\text{Ag}^+]) \text{ (left cell)}$$

$$\text{Ag(s)} \rightarrow \text{Ag}^+ + \text{e}^- \quad \mathcal{E} = -0.799\text{V} - (RT/F)\ln([\text{Ag}^+]/X_{\text{Ag}}) \text{ (right cell)}$$

Noting that $X_{Ag}=1$, and adding the two half-reactions we get

$$\begin{aligned}\Delta\epsilon &= - (RT/F) \ln(1/[Ag^+]_{left}) - (RT/F) \ln([Ag^+]_{right}) = (RT/F) \ln([Ag^+]_{left}/[Ag^+]_{right}) \\ &= (RT/F) \ln(0.01/0.1) = 0.591 * \ln(0.1) = -0.591 \text{ V}\end{aligned}$$

So there is a potential and the reaction goes in the opposite direction to how I have written it. That is, silver gets reduced at the right electrode and oxidized at the left.

5. (5 pts) In a cell we find that a particular signal transducing kinase, K, can exist in two forms, phosphorylated (K-P) and unphosphorylated (K). In fact, we find that during a critical growth phase of our cells, the phosphorylated form is the dominant form. However, experimentally we also find that the free energy of for this reaction with inorganic phosphate is:



What needs to happen in order to get this kinase phosphorylated in the cell? How is this most likely accomplished?

There are a number of answers to the questions but all must take into account that it is found that K-P is the dominant form. So adding a lot of inorganic phosphate is one way to make this reaction go but is probably not the way it's accomplished. There can be strange kinetic effects based on the influx of upstream reactions into K and the efflux from K-P, but you'd have to justify this well and show how it could occur. It is also unlikely given that K is a kinase and probably isn't consumed or destroyed by such reactions (except synthesis and proteolysis). (However, binding equilibria might explain it as well...) The most likely way is that this reaction is coupled to another set of reactions with *enough* negative free energy to overcome the 59 kJ/mol for this reaction. The easiest one to imagine is coupling to ATP hydrolysis. However, one would have to couple two ATP's to the reaction in order to overcome the free energy barrier. It is also not enough, necessarily, simply to place the other reactions in proximity to the kinase reaction...they really must be physically coupled. Kinase phosphorylation is coupled to ATP hydrolysis through actually reacting with ATP and abstracting a phosphate, usually facilitated by an enzyme.